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Diagonal and off-diagonal components of the self-diffusion tensor: their relation to and estimation from the NMR spin-echo signal

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Purpose: We derive an equation relating diagonal and off-diagonal elements of the apparent self-diffusion tensor, \( D \), to echo intensity in pulsed-gradient spin-echo experiments. With it we design pulse sequences to estimate all components of \( D \). This procedure is validated by diffusion NMR spectroscopy and imaging of isotropic and anisotropic media. We suggest that errors are made in ignoring off-diagonal elements of \( D \) in anisotropic diffusion experiments.

Principles: In isotropic media (e.g. water), a scalar self-diffusivity, \( D \), is the constant of proportionality between the gradient in concentration and the corresponding flux of labeled protons, \( v_c \), and their concentration gradients in orthogonal directions. The importance of these off-diagonal elements has not been appreciated, nor have they ever been measured.

Theory: Following Stejskal [1], magnetic field gradients and their integrals are defined as:

\[
G(t) = (G_x(t), G_y(t), G_z(t))^T; F(t) = G(t') \ 
\]

The echo attenuation by diffusion, \( A(TE)/A(0) \), is [1]:

\[
\ln \left( \frac{A(TE)}{A(0)} \right) = -\gamma^2 \int_0^{TE} (F(t) - 2\xi(t) t f) \ D(t') (F(t') - 2\xi(t') f) dt' \tag{2}
\]

where \( \gamma \) is the proton gyromagnetic ratio; \( \xi(t) \) is the Heaviside function, \( H(t-TE/2) \); and \( f = F(TE/2) \). When \( D \) is independent of time, Eq. (2) reduces to:

\[
\ln \left( \frac{A(TE)}{A(0)} \right) = -\sum_{i=1}^{3} \sum_{j=1}^{3} b_{ij} D_{ij} \tag{3}
\]

where the bi,j that are analogs to scalar b-factors [2], are calculated numerically or analytically for each sequence using Eq. (2). The b matrix is not necessarily symmetric.

Eq. (3) linearly relates the logarithm of the signal attenuation and each component of \( D \). We use multivariate linear regression (with weighted variances) to estimate optimally all components of \( D \) from measured echo intensities that are produced by field gradients applied in different directions.

Materials and Methods: Diffusion spectroscopy and imaging of water and pork loin samples were performed with a surface coil in a 4.7 T Spectrometer-Imager (GE Omega). Pulsed-gradient spin-echo sequences, incorporating symmetric trapezoidal gradient pulses (\( TR=15 \) s; \( TE=40 \) ms; pulse duration = 4 ms; rise time = 0.2 ms; pulse separation = 22.5 ms), were applied in seven non-collinear directions: \( (G_x, G_y, G_z) = ((0, 0, 1), (0, 1, 0), (0, 0, 1), (1, 0, 1), (1, 1, 0), (0, 1, 1), (1, 1, 1)) \). In each direction, three trials were performed in which gradient strength was increased from 1 to 14 or 15 G/cm in 1-G/cm increments. The total number of acquisitions, \( N \), was either 294 or 315.

Results: For water, the estimated \( D^{iso} \) ± S.E. (\( \rho^2 = 0.999999; N = 315 \)) at 14.0°C is:

\[
D^{iso} = (1.687 \pm 0.0020) \times 10^{-5} \ 
\]

The estimated \( D^{iso} \) ± S.E. (cm²/sec) for a pork loin sample at 14.5°C, whose grain was oriented nearly parallel to the x axis, (\( \rho^2 = 0.999999; N = 294 \)) is:

\[
D^{iso} = (10.137 \pm 0.530) \pm 0.008 \pm 0.007 \pm 0.006 \tag{5}
\]

The estimated \( D^{iso} \) ± S.E. (cm²/sec) for the same pork loin sample at 15.0°C, rotated 41° off the x axis in the x-z plane, (\( \rho^2 = 0.999999; N = 294 \)) is:

\[
D^{iso} = (-0.099 \pm 0.618) \pm 0.009 \pm 0.007 \pm 0.007 \tag{6}
\]

Discussion/Conclusion: The control experiment validates the method to estimate \( D \). Statistically significant differences among diagonal components of \( D \) demonstrate diffusion anisotropy in the pork loin sample. Small S.E. and \( \rho^2 \approx 1 \) show the multivariate linear model (Eq. (3)) fits the data faithfully; \( D \) is estimated with high significance.

In anisotropic diffusion, off-diagonal components of \( D \) vanish only when the "fiber" and "laboratory" frames of reference are coincident [3] - a condition which is rarely verifiable or satisfied. So, diagonal (and non-vanishing) off-diagonal elements of both \( b \) and \( D \) are assumed to affect the measured echo attenuation. As a corollary, at least six experiments are generally required to estimate six independent components of \( D \) in order to infer microscopic displacements of protons or tissue microstructure [3]. Omitting off-diagonal components of \( D \) in describing diffusion in anisotropic media also precludes determination of fiber orientation [3].

References: